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Role of substrate and transparent conducting oxide in impurity evolution in polycrystalline thin-film devices

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A comparison of as-grown and processed CdTe/CdS solar cell structures deposited on sapphire substrate has been undertaken with those grown on glass. The device structures were depth-profiled using quantitative secondary ion mass spectrometry. It was shown that while Si concentration profiles are similar to those for structures grown on glass, Na was more than one order of magnitude lower when sapphire was used instead of glass, showing that Na diffused from the glass. It was also found that there was no measurable diffusion of Sn from the SnO₂ layer into CdTe, and that the former played an important role in preventing the diffusion of In from In-containing transparent conducting oxide layer. Cl, O, Br, and F species were also investigated and while Cl and O were found to be independent of the nature of the substrate used, Br and F were shown to be affected by the processing. © 2005 American Institute of Physics. [DOI: 10.1063/1.2149990]

Float glass is widely used as substrate for the deposition of thin film solar cells, and at the same time very little is known about the effect of potential diffusion of impurities from the glass into the absorber and window layers of the devices. In recent reports,^{1–3} we have shown that for CdTe/CdS/transparent conducting oxide (TCO) solar cell structures grown on glass substrates, there is evidence of Si, O, and Na diffusion into the CdTe absorber layer from the glass. This was demonstrated using quantitative secondary ion mass spectrometry (SIMS) depth profiling, either from the CdTe surface down to the glass substrate, or from the TCO surface down to the CdTe layer after glass substrate removal, where these species were also found in the CdS window layer. F and Br are often used, respectively, during the growth of the TCO and/or the CdS layer, and in the bromine-methanol chemical etching of the structures prior to the back contact deposition, but again very few data are available in the literature regarding their effect on the final device.

In this letter, we report on a study of CdTe/CdS/TCO solar cell structures grown on sapphire substrates in order to avoid any contamination coming from the constituents of a glass substrate. The samples were depth profiled using quantitative SIMS analysis to reveal the concentration and distribution of the most important impurity elements that have a potential doping effect on both layers of the CdTe/CdS heterojunction. The data were compared with our previous findings from structures grown on glass substrates.^{1,2}

The SIMS was done from the CdTe side of the structures, and to avoid unnecessary contamination, the CdTe surfaces were not polished prior to SIMS profiling. The structures were grown on *c*-plane oriented and polished sapphire substrates of 5N purity. A TCO film consisting of indium tin oxide (ITO):F followed by SnO₂ was first deposited by reactive sputtering using respectively Ar+CHF₃+O₂ and Ar+O₂ ambient. The deposition temperatures were

450–480 °C for ITO-F and 450 °C for SnO₂. A CdS layer was then deposited by sputtering at 200 °C in Ar+CHF₃, and the CdTe layer was deposited by close space sublimation. The CSS growth of CdTe was performed in Ar ambient with a pressure of 100 mbar, and at temperatures of 540 °C and 750 °C for the substrate and source, respectively. The CdTe/CdS/SnO₂/ITO:F/sapphire structures were further processed with CdCl₂ heat treatment at around 400 °C in air, and chemically etched for 5 s in 10% bromine-methanol solution.

SIMS depth profiles of Si, In, Cl, Na, O, Sn, F, and Br were recorded on a Cameca IMS 4f using oxygen and cesium primary ion beams. Relative sensitivity factors (RSFs) for the CdTe layer were used to calibrate all the profiles recorded, and we will therefore limit our discussion of the quantitative SIMS data to the CdTe absorber layer of the solar cell structures although the data presented also allows a qualitative description of the distribution of impurities in the CdS window layer. RSFs for F and Br were extrapolated from HgCdTe SIMS standard while for all the remaining species the RSFs were extracted from CdTe single crystal implants.

Figure 1 shows the quantitative SIMS depth profiles of Na, Cl, Si, and O recorded from CdTe/CdS/SnO₂/ITO:F/sapphire structures as-grown (i.e., unprocessed) and following processing by CdCl₂ heat treatment (0.5 h in air) and bromine-methanol chemical etching. Na exhibited background levels of 6×10^{13} and 4×10^{16} cm⁻³ in the CdTe layer for unprocessed and processed structures, respectively. Na also had a clear declining profile in the as-grown sample versus the processed one. Similar behavior was found in as-grown structures on glass substrates as compared to processed structures, where the Na background concentrations were reported to be 10¹⁵ cm⁻³ increasing to 10¹⁷ cm⁻³ after processing.¹ Overall, the concentration of Na is lower in CdTe when a sapphire substrate is used compared to glass, and this, together with the diffusion-like profile, confirm that some of the Na present in CdTe was originating from the glass substrate during the CdTe growth.

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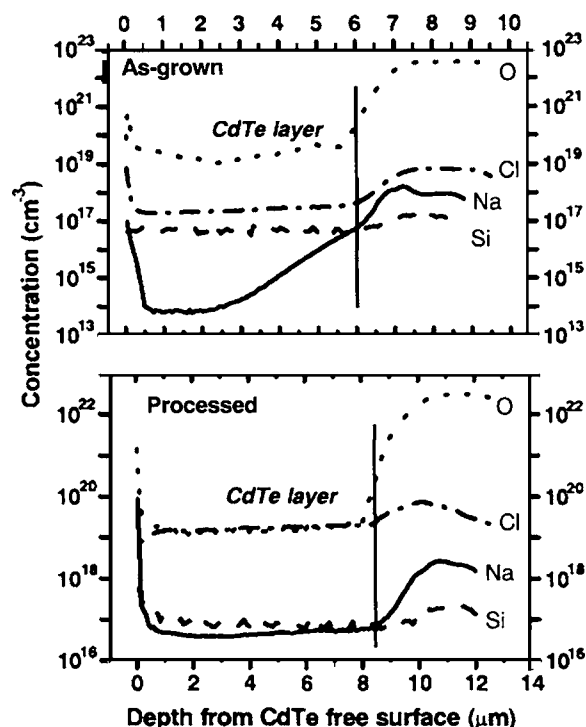


FIG. 1. Quantitative SIMS depth profiles of Na, Cl, Si, and O in as-grown and processed CdTe/CdS/SnO₂/ITO:F solar cell structures deposited on sapphire substrates. Although nominally identical in thickness, the depth scales are different for the as-grown and processed samples, and the vertical lines show the approximate location of the CdS/CdTe interface in both samples.

Upon processing, the concentration of Na increases and becomes more homogeneous within the CdTe; Na is a known contaminant in CdCl₂ (99.9% pure) used for the processing as we showed elsewhere.² Si however had almost the same level ($\sim 5 \times 10^{16} \text{ cm}^{-3}$) and profile shape before and after processing, and this is comparable to the concentration recorded ($\sim 4 \times 10^{16} \text{ cm}^{-3}$) for structures grown on glass.¹ Therefore the background level of Si does not seem to depend on the nature of the substrate used. O showed a constant background level in CdTe for the unprocessed as well as the processed samples, comparable overall to what was recorded for O in structures grown on glass.¹ With regard to the effect of the CdCl₂ treatment on the impurity profile within the structures, the concentration trends of Na, Si, and O, for unprocessed structures as compared to the processed ones, were in good agreement with our previously reported SIMS data from structures grown on glass and also with our inductively coupled plasma mass spectrometry (ICPMS) data recorded from the CdCl₂ powder used for the treatment of the structures.^{1,2} Cl had a flat profile in CdTe for both the unprocessed and processed samples, while its concentration in CdTe is about 100 times higher in the processed structures than in the as-grown ones. This comparison also shows that, following processing, a Cl depletion occurs in the region near the CdTe surface as compared to before processing, and this behavior was also noticed in the case of solar cell structures deposited on glass, and could be due to the chemical etching that follows the CdCl₂ treatment. It can therefore be concluded that, quantitatively as well as qualitatively, Cl has a similar trend independent of the substrate used.

The quantitative SIMS depth profiles of Br, F, Sn, and In for CdTe/CdS/SnO₂/ITO:F structures as-grown on sap-

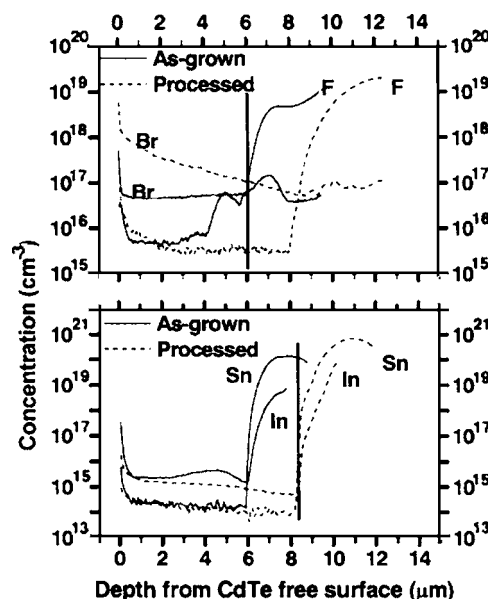


FIG. 2. Quantitative SIMS depth profiles of Br, F, Sn, and In for as-grown and processed CdTe/CdS/SnO₂/ITO:F solar cell structures deposited on sapphire substrates. Because of the difference in thickness, the CdTe/CdS interface is located at a depth of 6 μm and 8.5 μm for the as-grown and processed samples, respectively, as shown separately by the vertical lines.

phire substrates and following processing are shown in Fig. 2. Br showed a constant concentration of $4 \times 10^{16} \text{ cm}^{-3}$ in CdTe layer for unetched structures whilst for the etched structures the Br concentration in CdTe was at least ten times higher away from the CdTe surface, and reaches about 10^{18} cm^{-3} near the CdTe surface with a clear declining profile. It is therefore clear that upon etching with bromine-methanol solution, Br is introduced into the CdTe active layer. This effect has not been investigated before despite the fact that Br behaves as a donor in CdTe and is extensively used, in solution with methanol, for the chemical etching of the CdTe surface prior to the deposition of the back contact. F concentration was higher at the CdTe surface and in the first micron of the CdTe layer for both structures but more particularly for the processed one, as can be seen from Fig. 2. The rest of the profile was constant at $4 \times 10^{15} \text{ cm}^{-3}$ regardless of the structure. This suggests that F tends to segregate at the CdTe surface, and this segregation appears to be enhanced on processing. There is a peak of F in the CdS layer of the as-grown structure that results from the CHF₃ used during the CdS sputtering, and appears to anneal out during processing. Sn showed flat depth profiles in CdTe with a concentration of about 10^{14} cm^{-3} regardless of the structure (Fig. 2), indicating clearly that, like for the structures on glass,¹ Sn concentration and distribution are not influenced by the processing. Furthermore, the constant concentration of Sn also had the same value when In₂O₃:F was used as TCO instead of ITO:F/SnO₂, showing therefore that the main source of Sn in the CdTe is not the TCO. Depth profiles for In (Fig. 2) showed a concentration peak ($\sim 5 \times 10^{15} \text{ cm}^{-3}$) in CdTe near the interface with CdS for the as-grown structure. The processed structure had a concentration steadily increasing from $5 \times 10^{14} \text{ cm}^{-3}$ near the CdTe/CdS interface to $2 \times 10^{15} \text{ cm}^{-3}$ near the CdTe free surface. This shows that the distribution of In within the CdTe layer is clearly affected by the processing, and that some of the In detected in CdTe may well be due to the CdCl₂ treatment as an In level of about

10^{16} cm^{-3} was measured by ICPMS in the CdCl_2 powder used.² These In levels are low compared with the high In concentrations between $8 \times 10^{16} \text{ cm}^{-3}$ and 10^{17} cm^{-3} recorded in solar cell structures grown using $\text{In}_2\text{O}_3:\text{F}$ as TCO without SnO_2 layer, and attributed to an outdiffusion of In into CdTe from the $\text{In}_2\text{O}_3:\text{F}$ layer.^{1,2} In the present structures, the SnO_2 layer prevented In from diffusing into CdTe from the ITO:F layer.

The structures reported here had their CdTe layers grown using 6N purity CdTe source material, meaning that the total amount of impurity elements to be anticipated from a starting material of this grade is about $2 \times 10^{16} \text{ cm}^{-3}$. However, in the as-grown structures considered in this investigation, the concentrations found for Si, O, Br, and Cl are, as shown in the figures, higher than $2 \times 10^{16} \text{ cm}^{-3}$. This finding emphasizes the fact that even before undergoing any processing step, the structures have already some Si, O, Br, and Cl coming from impurity sources other than the CdTe starting material. Since these structures were all grown on sapphire (known for its stability at the temperatures used in this study) it is very unlikely that these impurity species are originating from the sapphire substrates. Therefore, the potential contamination sources are the growth chambers and environments used for the sputtering and the CSS deposition of the structure layers, together with the diffusion into the CdTe layer of elements from the other layers of the structure.

In conclusion, we have demonstrated that while Na originates from the glass, it is also introduced by processing with impure CdCl_2 . Si has a profile that is substrate independent and cannot be attributed to glass. As expected, Br is introduced by bromine-methanol etching and was shown to

be a potentially important contaminant. F is introduced by CHF_3 gas used during sputtering of ITO and CdS. Sn is not introduced from SnO_2 TCO, and SnO_2 is a barrier to In diffusion from ITO into CdTe. In does however come from both the TCO and from impurities in the CdCl_2 used for processing. The concentrations and profile shapes of O and Cl were not found to depend upon the substrate used.

The solar cell devices fabricated using the process described in this letter are reported and discussed in more detail elsewhere.⁴ Using a similar device fabrication process, Romeo *et al.*⁵ showed recently that cell efficiencies of up to 15.8% can be achieved, while a 14% efficiency was demonstrated by Gupta *et al.*⁶ for all-sputtered solar cells.

By comparing devices grown on sapphire and glass substrates using TCO layers of different nature, most of the issues discussed in this letter are relevant to a wide range of technologies that use TCO/glass as a large area low-cost substrate.

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